Can a double stranded DNA be unzipped by pulling a single strand?: Phases of adsorbed DNA

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We study the unzipping of a double stranded DNA (dsDNA) by applying an external force on a single strand while leaving the other strand free. We find that the dsDNA can be unzipped to two single strands if the external force exceeds a critical value. We obtain the phase diagram which is found to be different from the phase diagram of unzipping by pulling both the strands in opposite directions. In the presence of an attractive surface near DNA, the phase diagram gets modified drastically and shows richer surprises including a critical end point and a triple point.

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I. INTRODUCTION

DNA replication in prokaryotes gets initiated by unzipping of a few base pairs at one end of the dsDNA and then continues till end. These processes are assisted by various enzymes, often by exerting force on DNA [1]. It is now known theoretically, that a dsDNA undergoes an unzipping transition under the action of an external force if the force exceeds a temperature dependent critical value [2, 3, 4, 5]. Many studies of this unzipping transition [6, 7, 8, 9, 10] have revealed the importance of ensembles namely, the fixed distance and the fixed force ensemble [11]. For the fixed distance case, the distance between the strands is kept constant and the force required to maintain the distance is allowed to fluctuate, whose average is the quantity of interest, whereas, the average of the fluctuating distance between the strands where an external force is acting is the quantity of interest in the fixed force ensemble. For the single molecule studies, the results are known to depend on the ensemble used [5, 12]. The helicases work in both the fixed distance and the fixed force ensembles [13].

In recent years, the unzipping transition has been studied in detail with various extensions of the basic model. These include studies of models with intermediate phases [5, 10, 14, 15], dependence on pulling directions [16], models with additional features like semiflexibility [17], heterogeneity [9, 18, 19, 20, 21], saturation of hydrogen bonding [22], random forcing [23] etc. A similar problem of unzipping of an adsorbed polymer from the surface has also been studied [24, 25]. Experimental studies use various micro-manipulation techniques [26, 27, 28]. In all of these studies, the focus was on the breaking of the pairing by the external force. A more complicated situation emerges in DNA replication and segregation (e.g. in *Bacillus subtilis, E. Coli* etc.), where the membrane-DNA complexes play an important role [29, 30]. For example, in Bacillus subtilis, the DnaB protein has been shown to be a membrane-associated protein that is involved in initiation of replication [31]. Also, it is known that the interaction between the DNA and the membrane can form ordered domains [32]. Analogous laboratory situation would involve a substrate-DNA interaction. Recently atomic force microscopy has been used to identify the binding mechanism between the DNA and the DNA-binding agents by pulling one end of the dsDNA, which is immobilized on a gold surface in the presence of DNA-binding agents [33].

In this paper our aim is to study a simple model of unzipping of a dsDNA by applying an external force on a single strand in the transverse direction. Can a dsDNA be unzipped? Within the same framework, we also study the behaviour of the dsDNA in the presence of an attractive surface near it. This surface can mimic a membrane on which the DNA can be immobilized. Since adsorption of a polymer (here a dsDNA or a single strand of dsDNA) is a phase transition by itself (often critical), the competition between adsorption and unzipping is expected to add new features to the unzipping phase diagram.

The presence of the additional DNA substrate interaction both *in-vivo* and *in-vitro* system requires a different extension of the hitherto used models for the unzipping transition. A helical structure could pose extra problems for surface adsorption. In order to focus on the competition between adsorption and pairing, we use an extension of the Poland-Scheraga (PS) model [34] in two dimensions. Previous studies of DNA unzipping showed that the lattice model preserves, even in two dimensions, the basic results of DNA unzipping including the first order nature of the phase transition and the existence of a reentrant region [4]. For the problem at hand, we have also done Monte Carlo simulations in 2+1 dimensions, though without considering the helical structure of DNA, but the strands can wind together because of the dynamics, and find that the force-distance isotherms are qualitatively similar to the isotherms obtained in 1+1 dimensions.

At this point it is worthwhile to mention a few caveats of our approach. To achieve simplicity and tractability,

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we ignored the helical structure of dsDNA. The main obstacle in incorporating it is the absence as yet of any analytically tractable models for DNA melting that admits a helical ground state. In this situation, a PS type model serves as the starting point. We will see that if the base pairing energy of the DNA is greater than the binding to the surface, the unzipping of dsDNA by pulling a single strand takes place when it is away from the surface. Since the other strand of the DNA is left free, it can unwind itself from the pulled strand and the helical structure of the DNA can be safely neglected. However, in the opposite limit, the helical structure of the DNA becomes more and more crucial as the strength of binding to the surface is increased and its role can no longer be neglected. Another feature that may play an important role is the difference in the length per base pair of dsDNA and single-stranded DNA (ssDNA). Since it is difficult to incorporate this in a PS type lattice model considered in this paper, but can be done in continuous models, we ignore it in the present study.

Among the new features we find is the existence of a critical end point (CEP) [35], and the triple point [36] in the force versus temperature phase diagram for sufficiently strong attraction with the substrate. For weaker attraction, certain phases may not be thermodynamically stable. Some of the details of the CEP have been reported in a shorter paper [37]. Here we give all the necessary details and calculations and focus on the triple point. We use the generating function, the exact transfer matrix and Monte Carlo simulations to explore the equilibrium behaviour of this DNA-substrate system under a force on one strand.

The paper is organized as follows: In Sec. II, we define our model. Section III is devoted to two extreme limits in which the problem reduces to the unzipping of adsorbed polymer from a straight and a zig zag hard-wall. These results are used in the subsequent sections. As a prelude to the substrate interaction problem in hand, we also need to consider the case of unzipping of a ds-DNA strand. In Sec. IV, we review the unzipping of a dsDNA by pulling its strands in opposite directions. The unzipping by pulling a single strand is studied in Sec. V. In Sec. VI, the unzipping of an adsorbed DNA by pulling a single strand is studied. The existence of a triple point [36] and a critical end point are shown here. There occurrences are not dependent on each other. These emerges as the relative attraction of the substrate is made stronger. In addition to providing some details on CEP this section focuses on the triple point. Finally, we draw our conclusions in Sec. VII.

II. MODEL

We model the DNA by two directed self avoiding walks (DSAWs) on a $D = 1+1$ dimensional square lattice. The walks, starting from the origin, are directed along the diagonal of the square (z direction). The walks are not allowed to *cross each other* but whenever they meet (i.e. $x_1 = x_2$) there is a gain in energy $-\epsilon_b(\epsilon_b > 0)$ for every contact. At the diagonal ($x = 0$) there is an impenetrable attractive surface, with an energy $-\epsilon_w(\epsilon_w > 0)$, which favors adsorption of the DNA. In $1 + 1$ dimensions, the surface is a line passing through the diagonal of a square lattice, and only one of the strands can get adsorbed on it (i.e. $x_1 = 0$), since the two strands of the DNA cannot cross each other. One end of the DNA is always kept anchored at the origin. We apply an external force g, along the transverse direction (x-direction) on the free end of one of the strands of the DNA. The other strand is left free. Henceforth, the strand which is left free is called the "free strand" and the strand, on which the external force acts is called the "pulled strand". A schematic diagram of the model in $1 + 1$ dimensions is shown in Fig. 1. In $2+1$ dimensions, the surface is a plane passing through the diagonal of a cubic lattice. Unlike the $1 + 1$ dimensional case, both the strands of the DNA can get adsorbed on the surface and still satisfy the non-crossing constraint on the plane (y-direction). In this paper we concentrate only on $1 + 1$ dimensional case.

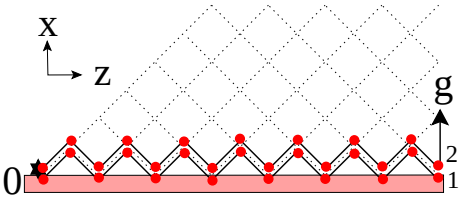

FIG. 1: Schematic diagram of a dsDNA adsorbed on the surface (shaded region) in $1 + 1$ dimensional square lattice. There is a binding energy $-\epsilon_b$ between bases (shown by filled circles) of the strands of the DNA. One end of the DNA is always kept anchored on the surface at the origin (shown by star). The free strand (denoted by 1) can gain energy $-\epsilon_w$ for every contact with the surface (i.e., $x_1 = 0$). An external force g (shown by arrow) is applied at the free end of the pulled strand (denoted by 2) in the transverse direction.

Let $D_n(x_1, x_2)$ be the partition function (temperature dependence not shown explicitly) of a dsDNA in the fixed distance ensemble where nth monomers of the strands are at positions x_1 (free strand) and x_2 ($x_2 \geq x_1$) (pulled strand) respectively from the wall. $D_n(x_1, x_2)$ satisfies the recursion relation

$$D_{n+1}(x_1, x_2) = \sum_{i,j=\pm 1} D_n(x_1 + i, x_2 + j) \times [1 + \mathcal{W}\delta_{x_1,0}]\,[1 + \mathcal{B}\delta_{x_2,x_1}]\,, \quad (1)$$

where $\mathcal{W} = (e^{\beta\epsilon_w} - 1)$, $\mathcal{B} = (e^{\beta\epsilon_b} - 1)$ and $\beta = 1/T$ is the inverse temperature in units of $k_B = 1$, with the initial condition $D_0(x_1, x_2) = (e^{\beta\epsilon_w}\delta_{x_1,0})(e^{\beta\epsilon_b}\delta_{x_2,0})$. The impenetrability of the surface and the non-crossing of the strands demand $x_2 \geq x_1 \geq 0$. The canonical partition function with an external force g at the end of the pulled strand is then obtained by summing over all the allowed

configurations of the DNA of length N on the lattice.

$$Z_N(\beta, g) = \sum_{x_2 \geq x_1 \geq 0} D_N(x_1, x_2)\ e^{\beta g x_2}, \tag{2}$$

where $e^{\beta g x_2}$ is the Boltzmann weight due to the force g.

From x_1 and x_2, one can define the relative coordinate x, and the center of mass coordinate X as

$$x = x_2 - x_1, \qquad X = \frac{1}{2}\left[x_1 + x_2\right]. \tag{3}$$

The relative coordinate contains all the necessary information of the unzipping transition of a dsDNA when its strands are pulled in the opposite directions [2, 4, 6, 9]. For the single strand pulling case we need both the relative and the center of mass coordinate to track the chains individually.

A. Quantities of Interest

The following physical quantities are of interest:

1. The average distances of the end monomers of both strands from the surface, which are defined as

$$\langle x_i \rangle = \sum_{x_2 \geq x_1 \geq 0} \frac{x_i\ D_N(x_1, x_2)\ e^{\beta g x_2}}{Z_N(\beta, g)}, \tag{4}$$

   where $\langle \cdots \rangle$ denotes the thermal averaging and subscript $i = 1$ and $i = 2$ stand for the free and the pulled strand respectively. The summation is taken over all the allowed configurations. The positions of end monomers give us the information needed to characterize the phase of the system.

2. The response to the force, i.e. the isothermal extensibility, which can be expressed, for both strands, in terms of fluctuations of the position of end monomers

$$\chi_i = \left.\frac{\partial \langle x_i \rangle}{\partial g}\right|_T = \frac{1}{k_B T}\left[\langle x_i^2 \rangle - \langle x_i \rangle^2\right], \quad (i = 1 \text{ or } 2). \tag{5}$$

Equations (4) and (5) are useful to obtain the above physical quantities numerically.

III. UNZIPPING AN ADSORBED POLYMER

Let us first study the two extreme limits: (i) $\epsilon_{\rm b} \to \infty$ and $\epsilon_{\rm w}$ is finite (and we take $\epsilon_{\rm w} = 1$), and (ii) $\epsilon_{\rm w} \to \infty$ and $\epsilon_{\rm b}$ is finite ($\epsilon_{\rm b} = 1$). For the former case, the two strands of the DNA always stay together for the entire range of temperature in which we are interested. In such a situation, an external force g on the pulled strand also pulls the free strand. Therefore, the DNA can be equivalently represented by a single polymer in the center of mass frame. The problem then reduces to the unzipping of an adsorbed polymer on an straight impenetrable surface (hard-wall). However, for case (ii), the free strand remains adsorbed on the surface and itself acts as a zig zag hard-wall for the pulled strand. In this section, we obtain the phase diagram for both the cases.

A. Straight hard-wall

In the fixed distance ensemble, the partition function $w_n(x)$ of a dsDNA in the center of mass frame satisfies the recursion relation

$$w_{n+1}(X) = \left[w_n(X+1) + w_n(X-1)\right]\left[1 + \mathcal{W}\delta_{X,0}\right]. \tag{6}$$

Note that while writing Eq. (6) from Eq. (1) we have absorbed the Boltzmann factor $e^{\beta\epsilon_{\rm b}}$ in $w_n(X)$. The partition function in the presence of an applied external force g is then given by

$$Z_N(\beta, g) = \sum_{X \geq 0} w_N(X)\ e^{\beta g X}. \tag{7}$$

This problem has been studied in recent years because of its similarity with the DNA unzipping [24, 25]. It is known that the polymer unzips from the surface if the force exceeds a critical value. Below this critical force, the polymer remains adsorbed on the surface while above it the polymer is in the desorbed phase. The phase boundary separating the two phases is given by

$$g_{\rm c}^{(s)}(T) = \frac{T}{2}\ln\left[e^{\beta\epsilon_{\rm w}} - 1\right]. \tag{8}$$

and is shown in Fig. 2 by a solid line. The triangles on the line represent the phase boundary obtained numerically by using the exact transfer matrix. The method is introduced below for the zig zag surface. Here we have taken $\epsilon_{\rm w} = 1$. The critical force decreases monotonically with the increase of temperature and becomes zero at

$$T_{\rm c}^{(s)} = \epsilon_{\rm w}/\ln 2, \tag{9}$$

where the polymer desorbs from the surface because of the thermal fluctuations.

B. Zig zag surface

The recursion relation for the partition function $b_n(x_2)$ of the pulled strand, in the fixed distance ensemble, can be written as

$$\begin{aligned} b_{n+1}(x_2) \ &= \ \left[b_n(x_2+1) + b_n(x_2-1)\right] \\ &\quad \times \left[1 + \mathcal{B}\delta_{x_2,0}\right]\left[1 + \mathcal{B}\delta_{x_2,1}\right]. \end{aligned} \tag{10}$$

Note that the above recursion relation differs from Eq. (6) in the extra factor due to the binding of the odd monomers to the wall. In Eq. (6), only the even

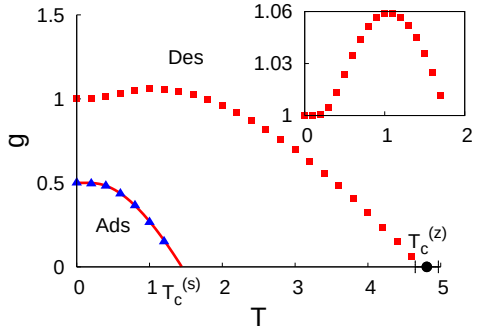

FIG. 2: g vs T phase diagram for the unzipping of an adsorbed polymer from an attractive impenetrable surface. The points are obtained by using the exact transfer matrix and the solid curve is an analytical result (see Eq. (8)). The triangles and squares represent the phase boundary between the adsorbed (Ads) and the desorbed (Des) phases for the straight and zig zag hard-walls respectively. The thermal desorption temperatures for the straight and the zig zag surfaces are shown respectively by $T_c^{(s)}$ and $T_c^{(z)}$. For the later case it is shown by a circle.

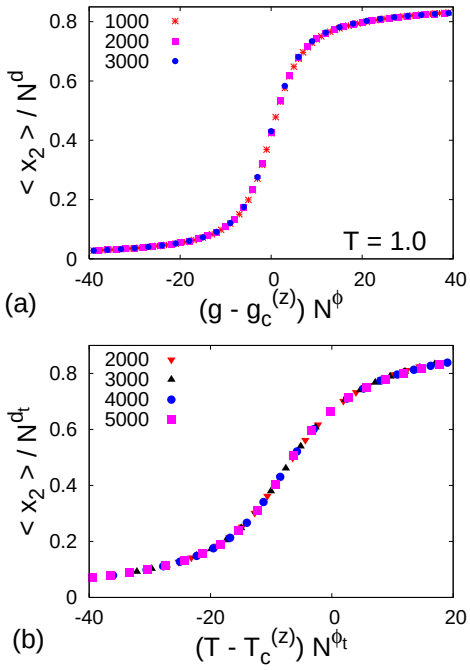

FIG. 3: Data collapse of the average distance $\langle x_2 \rangle$ of the last monomer from the zig zag surface (a) as a function of g at $T = 1.0$ for $N = 1000$, 2000 and 3000. The critical exponents are $d = 0.99 \pm 0.01$ and $\phi = 1.0 \pm 0.01$ and the critical force $g_c^{(z)} = 1.059 \pm 0.001$. (b) as a function of T for $N = 2000$, 3000, 4000 and 5000. In this case the critical exponents are $d_t = 0.53 \pm 0.03$, $\phi_t = 0.4 \pm 0.03$ and $T_c^{(z)} = 4.81 \pm 0.16$.

monomers bind to the surface. This modification is enough to make a difference in the phase diagram. This extra energy affects the intermediate temperature behaviour of the polymer as it becomes energetically costly to create bubbles on the polymer adsorbed on a zig zag hard-wall. This can be understood as follows: The ground state for the polymer adsorbed on a straight hard-wall contains inherent bubbles of length $\ell = 2$ because the geometry of the problem allows only $N/2$ monomers on the wall. In contrast, for the zig zag hard-wall there are no such inherent bubbles as all the N monomers are adsorbed on the wall. To create a bubble of length $\ell = 2$, one of the monomers has to come out from the wall which costs energy. Furthermore, getting larger bubbles are easier for the polymer adsorbed on the straight hard-wall than the zig zag case. For example, flipping of one monomer from the wall can create a bubble of length $\ell = 4$ for the normal hard-wall, while three consecutive monomers have to come out from the wall for the zig zag case to create a bubble of the same size.

Under the influence of a fixed pulling force g at the free end, the partition function is obtained by

$$\mathcal{Z}_N(\beta, g) = \sum_{x_2} b_N(x_2) e^{\beta g x_2}. \tag{11}$$

The partition function of the chain length N is obtained numerically, at a given temperature, by iterating Eq. (10) and, then, for various force g by using Eq. (11). This is known as the exact transfer matrix technique. The distance of the end monomer of the pulled strand from the surface, which is the quantity of interest, is obtained by using

$$\langle x_2 \rangle = \frac{1}{\mathcal{Z}_N(\beta, g)} \sum_{x_2} x_2 b_N(x_2) e^{\beta g x_2}. \tag{12}$$

In Fig. 3(a), we have shown the data collapse of g vs $\langle x_2 \rangle$ isotherms at $T = 1.0$ for the chain of lengths $N = 1000$, 2000 and 3000. We have used the scaling form

$$\langle x_2 \rangle = N^d \mathcal{Y}\left((g - g_c^{(z)}) N^{\phi}\right), \tag{13}$$

where d and ϕ are the critical exponents and $g_c^{(z)}$ is the critical force. By using the Bhattacharjee-Seno procedure [38], we obtained $g_c^{(z)} = 1.059 \pm 0.001$, $d = 0.99 \pm 0.01$ and $\phi = 1.0 \pm 0.01$. These exponents are same as the exponents obtained for the unzipping from the straight hard-wall [24] and the DNA unzipping problem [4, 6]. We use same procedure at various temperatures to obtain the phase diagram.

The phase diagram of unzipping from the zig zag surface is shown in Fig. 2 by points for $\epsilon_b = 1$. If we compare this with the phase boundary for the straight surface, we see that at very low temperatures ($T = 0$), the force required to unzip the polymer from the zig zag surface is twice that from the normal surface since one has to overcome an additional binding at $x_2 = 1$. This implies the low temperature behavior of the polymer is same for both the walls i.e. $g \propto \epsilon$ ($\epsilon = \epsilon_w$ for the straight surface whereas $\epsilon = 2\epsilon_b$ for the zig zag case). The polymer starts behaving differently as temperature is increased. As already mentioned, it is easy to create a bubble on the

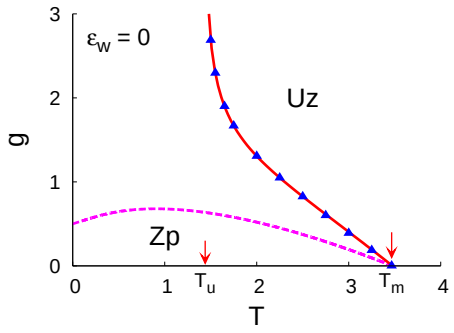

FIG. 4: g vs T phase diagram for the DNA unzipping. The dashed line represents the phase boundary for the unzipping by pulling strands in opposite directions by an external force force g. The solid line is exact phase boundary (Eq. (24)) and the triangles are from the numerics for the pulling of a single strand for which the transition takes place only above a minimum temperature $T_{\rm u}$.

polymer adsorbed on the straight wall, whereas more energy is needed to create a bubble of the same size on the polymer adsorbed on the zig zag surface. For the straight surface, the critical force needed to unzip the polymer from the wall decreases monotonically with the temperature. In contrast, for the zig zag surface, the critical force increases at intermediate temperatures, reaches to a maximum value and then decreases to zero, thus showing reentrance as shown in the inset of Fig. 2. To obtain the desorption temperature for the zig zag case, we resort again to the finite size scaling (but with temperature as a variable) of the form

$$\langle x\rangle = N^{d_t}\mathcal{Y}\left((T-T_{\rm c}^{(z)})N^{\phi_t}\right), \tag{14}$$

with $T_{\rm c}^{(z)}$ as the critical desorption temperature and d_t and ϕ_t are the critical exponents. The data collapse, for chain lengths $N = 2000$, 3000, 4000 and 5000, obtained for $d_t = 0.53\pm0.03$, $\phi_t = 0.4\pm0.03$ and $T_{\rm c}^{(z)} = 4.81\pm0.16$ is shown in Fig. 3(b), and the desorption temperature $T_{\rm c}^{(z)}$ is shown in Fig. 2 by a solid circle.

IV. UNZIPPING DNA BY PULLING STRANDS IN OPPOSITE DIRECTIONS

Before considering the unzipping by pulling a single strand, let us first concentrate on the unzipping of a ds-DNA by pulling its strands in opposite direction by an external force g. This problem has received a lot of attention in recent years due to its resemblance with the way the DNA unzipping experiments are done [26, 28].

In the fixed distance ensemble, the partition function of the dsDNA can be obtained by assigning $\epsilon_{\rm w} = 0$ in Eq. (1). The recursion relation, in the relative coordinate, reads as [6]

$$d_{n+1}(x) = [d_n(x+1) + 2d_n(x) + d_n(x-1)]\,[1+\mathcal{B}\delta_{x,0}], \tag{15}$$

with the initial condition $d_0(x) = e^{\beta\epsilon_{\rm b}}\delta_{x,0}$.

In the fixed force ensemble, the partition function for the DNA of length N, is then obtained by

$$Z_N(\beta,g) = \sum_{x\geq 0} d_N(x)\; e^{\beta g x}. \tag{16}$$

The phases of the DNA and the transition come from the singularities of the of the generating function

$$\mathcal{G}(z,\beta,g) = \sum_{N=0}^{\infty} z^N Z_N(\beta,g). \tag{17}$$

The singularities are [4, 6]

$$z_1 = \frac{1}{4}, \tag{18a}$$

$$z_2(\beta,\epsilon_{\rm b}) = \sqrt{1-e^{-\beta\epsilon_{\rm b}}} - 1 + e^{-\beta\epsilon_{\rm b}}, \tag{18b}$$

and

$$z_3(\beta,g) = \frac{1}{2+2\cosh\beta g}. \tag{18c}$$

The phase of the DNA is given by the singularity which is closest to the origin and the phase transition takes place when the two singularities cross each other. For low force, $z_2(\beta,\epsilon_{\rm b})$ is closest to the origin and the DNA is in the zipped phase (double-stranded), while for high force, $z_3(\beta,g)$ becomes closest and the DNA is in the unzipped phase (two single strands). The force-temperature phase boundary between the two phases is obtained by equating the two singularities, which gives [5, 6]

$$\begin{aligned} g_{\rm c}(T,\epsilon_{\rm b}) &= \frac{T}{2}\cosh^{-1}\left[\frac{1}{2z_2(\beta,\epsilon_{\rm b})}-1\right] \\ &= -\frac{T}{2}\ln\lambda\left(z_2(\beta,\epsilon_{\rm b})\right), \end{aligned} \tag{19}$$

where $\lambda(z) = (1-2z-\sqrt{1-4z})/(2z)$. The thermal denaturation (melting), coming from $z_1 = z_2(\beta,\epsilon_{\rm b})$, is at

$$T_{\rm m} = \epsilon_{\rm b}/\ln(4/3). \tag{20}$$

The phase boundary separating the zipped phase (Zp) from the unzipped phase (Uz) is shown by the dashed line in Fig. 4.

V. UNZIPPING DNA BY PULLING A SINGLE STRAND

In previous sections, we have seen that the finite size scaling of the force-distance isotherms (or the extensibility), obtained by using the exact transfer matrix for

various chain lengths, can be used to obtain the phase diagrams numerically. We use Eqs. (1) and (2) with $\epsilon_{\rm w} = 0$ to obtain the partition function of a dsDNA of length N. The average distances of the end monomers of both the strands from the surface is obtained by using Eq. (4).

Alternatively, using the fact that the force is only on one of the strands and the surface plays no role in the phase boundary, the partition function can be obtained, in the relative coordinates, by the following recursion relation (in a mixed fixed-distance-force ensemble)

$$d_{n+1}(x) = \left[d_n(x+1)\ e^{\beta g} + d_n(x)\ e^{\beta g} + d_n(x)\ e^{-\beta g} + d_n(x-1)\ e^{-\beta g}\right]\left[1 + \mathcal{B}\delta_{x,0}\right], \tag{21}$$

with the initial condition $d_0(x) = e^{\beta\epsilon_{\rm b}}\delta_{x,0}$. The above recursion relation can be analyzed analytically and the boundary separating the zipped and the unzipped phases can be obtained exactly. The details of the calculation are given in Appendix A.

A. Isotherms and Extensibility

The force-distance isotherms at $T = 0.5$ and 1.5 are shown in Fig. 5(a). Due to the entropic repulsion, the dsDNA stays at a distance of $\sqrt{N}$ from the surface, even for $g = 0$, to maximize its entropy (see Fig. 5(b)). When the pulling force, g, is small, the binding energy, $\epsilon_{\rm b}$, wins over the entropy, which the free strand can gain if it separates itself from the pulled strand, and the dsDNA as a whole gets stretched in the direction of the force. The average distances of end points of the strands from the surface, $\langle x_{1,2}\rangle/N$, remain the same (for both the strands) and increase linearly with g. The slope, however, depends on the temperature; it is larger at low temperatures and smaller at high temperatures. As g is increased further, the dsDNA gets completely stretched at $T = 0.5$. But for $T = 1.5$, before the dsDNA can get fully stretched, a critical force $g_{\rm u}$ is reached, and the free strand of the DNA gets unzipped from the pulled strand to increase its entropy. We call this as "transition Uz". This transition can be studied in the relative coordinate, x, defined in Eq. (3). Below $g_{\rm u}$, the strands stay together ($\langle x\rangle/N \to 0$ as $N \to \infty$), and above it, they are maximally separated ($\langle x\rangle \sim N$).

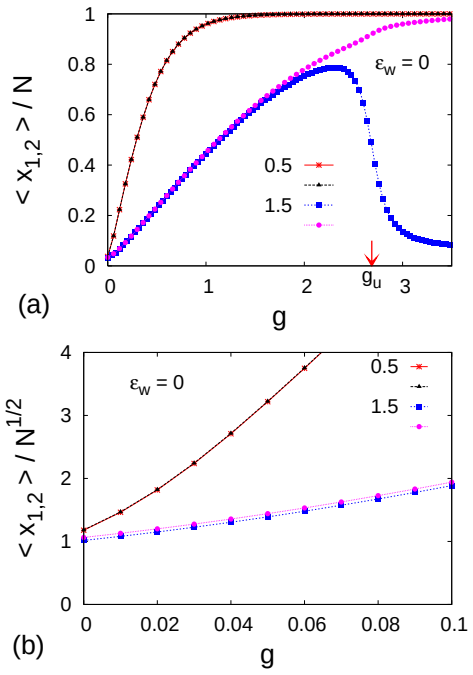

FIG. 5: (a) g vs $\langle x_{1,2}\rangle/N$ isotherms at $T = 0.5$ and 1.5 for $\epsilon_{\rm w} = 0$. The squares and circles refer to the two different strands of the dsDNA. The critical force above which the dsDNA unzips is shown by $g_{\rm u}$. In (b) same isotherms are shown near $g = 0$ in a different scale $\langle x_{1,2}\rangle/N^{1/2}$. The broken lines are a guide to the eyes.

The isothermal extensibility, obtained by using Eq. (5), is plotted in Fig. 6(a) as a function of g for various chain lengths at $T = 1.5$. The critical force $g_{\rm u}$ can be located by using the finite size scaling of the form

$$\chi = N^d \mathcal{G}\left((g - g_{\rm u})\ N^{\phi}\right), \tag{22}$$

with d and ϕ as critical exponents. By using the Bhattacharjee-Seno procedure, we obtained $d = 2.02 \pm 0.01$, $\phi = 1.01 \pm 0.01$ with $g_{\rm u} = 2.692 \pm 0.001$. These exponents are same as the exponents for the DNA unzipping by pulling strands in the opposite directions [4, 6, 10]. This indicates that, similar to the later case, the unzipping by pulling a single strand is also a first order phase transition with

$$\chi/N \ \sim\ |\ g - g_{\rm u}\ |^{-1}\ . \tag{23}$$

The data collapse is shown in Fig. 6(b). The finite size scaling of extensibility, as described above, can be used at various temperatures to obtain the phase diagram of unzipping.

B. Phase Diagram

The boundary separating the zipped (Zp) and the unzipped (Uz) phases is given by (see Appendix A for de-

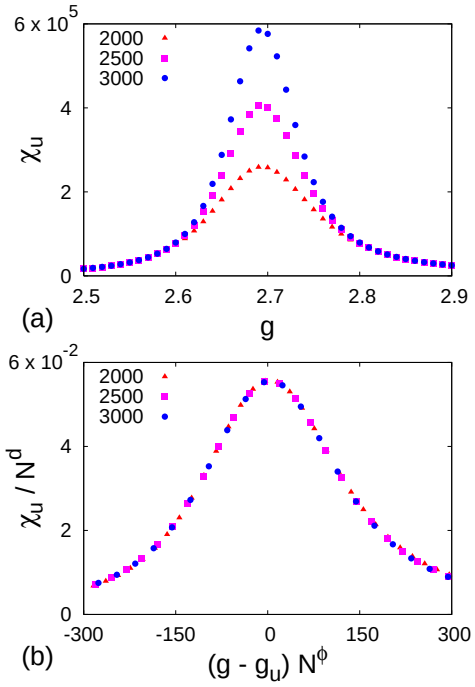

FIG. 6: (a) Isothermal extensibility χ_u vs g at $T = 1.5$ for the DNA of lengths $N = 2000$, 2500 and 3000. (b) The data collapse of the extensibility. For all plots $\epsilon_b = 1$.

tails)

$$g(T) = \frac{k_B T}{2} \ln\left(\frac{2e^{-\beta\epsilon_b} - 2}{1 - 2e^{-\beta\epsilon_b}}\right). \qquad (24)$$

The same phase boundary has also been obtained by Marenduzzo *et al.* [39] in a different context of melting of a stretched DNA. The phase boundary is shown in Fig. 4 by a solid line which matches excellently with the results (triangles) obtained numerically from the exact transfer matrix. The plot shows that in contrast to pulling both the strands in opposite directions, where, below the melting temperature, the DNA can be unzipped at all temperatures including $T = 0$, the DNA can only be unzipped above a certain temperature T_u ($T_u = \epsilon_b/\ln 2$) for the single strand pulling. Below T_u, the DNA remains in the zipped phase for any value of force g. The melting temperature of the dsDNA remains the same, i.e. $T_m = \epsilon_b/\ln(4/3)$, because in our model the force acts in the transverse direction and does not overstretch the DNA. Recently it was found that a longitudinal stretching force on one of the strand destabilize the DNA which results in a reduced melting temperature [40, 41, 42, 43].

The origin of the unzipping transition by pulling a single strand is different from the unzipping transition by pulling both the strands. For the latter case, the transition sets in due to the competition between the base pairing energy ϵ_b, which binds the complementary bases (or monomers) of two strands, and the orientation of the individual links connecting the monomers. In contrast, the interplay between the binding energy ϵ_b, and the entropy, which the free strand can gain if it is in the unzipped phase, is responsible for the single chain case. When $T < T_u$, the binding energy wins over the entropy and the DNA remains in the zipped phase for any value of g. For large g, the DNA takes a fully stretched configuration and bubbles are not possible. This is analogous to the Y model studied in Ref. [6]. In this model, the thermal melting of dsDNA takes place at $T_u = \epsilon_b/\ln 2$ and the transition is of first order [6]. For $T < T_u$, the DNA always remains in the zipped phase. For $T > T_u$, the free strand has all the favourable conditions to increase its entropy. Therefore, as T is increased, the free strand can get separated from the pulled strand well below the fully stretched configuration and the critical force g_u falls rapidly with increasing the temperature, becoming zero at T_m.

There are other factors that also contribute in the unzipping of dsDNA by pulling a single strand but neglected in our lattice model. An important one is the fact that the length per base pair of the dsDNA and the ssDNA are different (0.34nm and around 0.5mn respectively). If the applied force is low, the dsDNA has larger extension than the ssDNA and the dsDNA remains stable. However, for sufficiently strong force, the extension of ssDNA becomes more than the dsDNA and the force destabilize the dsDNA and favors its unzipping [40]. It is difficult to incorporate this in a lattice model like ours, but we believe that it can be done in a continuous description of the model. It would be interesting to study the combined effect of both mechanisms in DNA unzipping by pulling a single strand as this could bring down T_u.

VI. UNZIPPING AN ADSORBED DNA

Let us now consider the complete model of an attractive surface (i.e., $\epsilon_w > 0$) near a dsDNA. Here the free strand of the DNA experiences two different energies of opposite tendencies even at $T = 0$. The energy ϵ_w tries to keep the free strand adsorbed on the surface while the binding between the strands, ϵ_b, tries to keep it with the pulled strand. For $T > 0$, the entropy also plays a role and the competition among them makes the phase diagram very rich. We establish the possibility of four distinct phases (I) Z_a: zipped DNA adsorbed on the surface, (II) Z_d: zipped DNA desorbed from the surface, (III) U_{ad}: unzipped DNA with the free strand adsorbed on the surface, and (IV) U_{dd}: unzipped DNA with both the strands desorbed from the surface.

A. Isotherms and Extensibility

In Fig. 7, we have shown the force-distance isotherms for $\epsilon_w = 1.0$, 1.8 and 2.0 at two different temperatures $T = 0.5$ and 1.5 for the chain of length $N = 1000$. The values of ϵ_w and T are selected to display the typical characteristics of the phase diagrams. The phase dia-

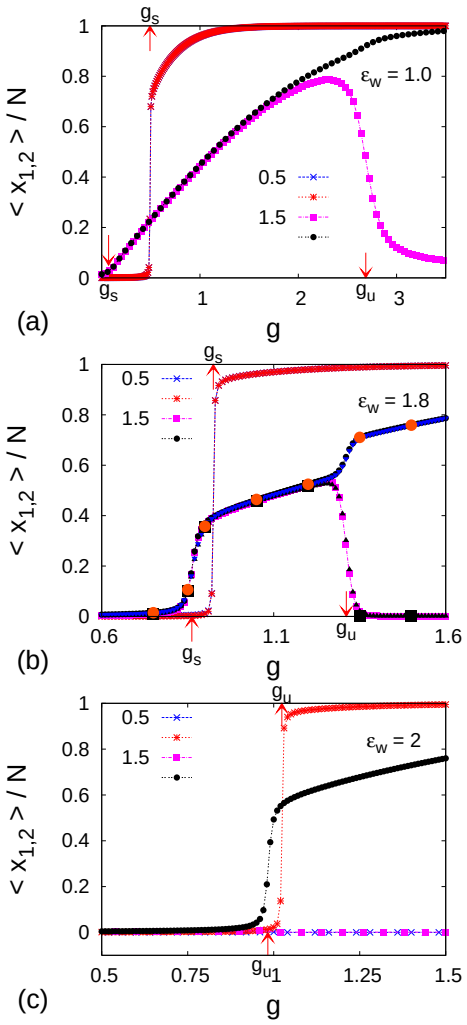

FIG. 7: The $\langle x_{1,2}\rangle/N$ vs g isotherms at temperatures, $T = 0.5$ and 1.5 for various $\epsilon_{\rm w}$. All isotherms are for $N = 1000$ with $\epsilon_{\rm b} = 1$. The transitions Uz and Sz take place at critical forces g_u and g_s respectively (see text). These are shown by arrows in the plot. (a) For $\epsilon_{\rm w} = 1$, (b) For $\epsilon_{\rm w} = 1.8$. We have also shown the averages obtained by using Monte Carlo simulations. The squares and circles refer to the two different strands of the dsDNA. The upper and the lower triangles are the estimates given by the multiple histogram technique at various g. (c) For $\epsilon_{\rm w} = 2$. The broken lines are a guide to the eyes.

grams are obtained by repeated use of finite size scaling of the response function.

For $\epsilon_{\rm w} = 1.0$, the isotherms are shown in Fig. 7(a). In the absence of a force g, the ground state is an adsorbed DNA on the surface. As g is increased, we see that there is a critical force, $g_{\rm s}$, at which the DNA gets unzipped from the surface but remains double stranded. We call this as "transition Sz". This involves the center of mass coordinate, X, given by Eq. (3). Below $g_{\rm s}$, $\langle X\rangle/N = 0$ as $N \to \infty$, but it takes a finite (non-zero) value above $g_{\rm s}$. When g is increased further, the dsDNA stretches more and more in the direction of the force, and takes a fully stretched configuration for $T = 0.5$. However, for $T = 1.5$, the free strand gets separated from the pulled strand (transition Uz) at $g_{\rm u}$ and stays at a distance of $\sqrt{N}$ from the surface (see Fig. 7(a)).

The isotherms for $\epsilon_{\rm w} = 1.8$ is shown in Fig. 7(b). At $T = 0.5$, the isotherm is similar to that of $\epsilon_{\rm w} = 1$, though with a higher critical force $g_{\rm s}$. It is different for $T = 1.5$, where, on increasing the force g, the transition Sz takes place at $g_{\rm s}$. On increasing g further, we have an another transition Uz at $g_{\rm u}$, where the free strand separates itself from the pulled end and gets adsorbed on the surface. We have obtained the isotherm at $T = 1.5$ by two different methods. The smaller symbols with broken lines between them are from the exact transfer matrix whereas, the bigger symbols (squares and circles representing the two strands of the DNA) are obtained by performing Monte Carlo simulations, at their respective g values. We also collect histograms, $h_k(E, x_1, x_2)$ (E is the total binding energy, x_1 and x_2 are respectively the distances, from the surface, for the free and the pulled strand, and the subscript k, stands for the simulation performed at force g_k) at each simulation. These histograms are then combined to estimate $\langle x_{1,2}\rangle$ for a range of forces by using the multiple histogram technique [44]. The estimates, so obtained, are shown by the upper and the lower triangles for the free and the pulled strand respectively in Fig. 7(b). The isotherm obtained from both the methods agree excellently. The details of the Monte Carlo simulation is discussed in Appendix B. Our Monte Carlo simulations in $2+1$ dimensions also shows similar results [37].

The isotherms for $\epsilon_{\rm w} = 2$ are shown in Fig. 7(c). The plot shows that the only possible transition is the unzipping of the dsDNA to two single strands (i.e. the transition Uz) at $g_{\rm u}$, because the free strand minimizes its energy by staying adsorbed on the surface.

The critical force $g_{\rm s}$ at which the transition Sz takes place is obtained by the finite size scaling of isothermal extensibility as given by Eq.(22). A good data collapse is obtained for the exponents $d_{\rm s} = 1.95\pm0.05$ and $\phi_{\rm s} = 1.0\pm 0.01$ showing that, as for transition Uz, the transition Sz is also first order. We use the finite size scaling of extensibility at various temperatures to obtain the phase diagrams.

B. Phase Diagram

The discussions in the previous subsection reveal that there are four possible phases for the problem at hand. These are:

1. *Phase I* — The zipped DNA (i.e., dsDNA) adsorbed on the surface. This phase is characterized by $\langle x_{1,2}\rangle/N \to 0$ as $N \to \infty$. *This phase is called* $\rm Z_a$.

2. *Phase II* — The dsDNA desorbed from the surface. In this phase we have $\langle x_{1,2}\rangle/N \to A$ $(0 < A \leq 1)$ as $N \to \infty$. *This phase is called* $\rm Z_d$.

3. *Phase III* — In this phase, the DNA is unzipped (i.e., the strands stay away from each other). The pulled strand is stretched in the direction of the force and the free strand is adsorbed on the surface. This phase is characterized by $\langle x_1\rangle/N \to 0$ but $\langle x_2\rangle/N \to 1$ as $N \to \infty$. *This phase is called* $\mathrm{U_{ad}}$.

4. *Phase IV* — In this phase both the strands stay away from the surface as well as from each other. The pulled strand follows the pulling force as in *phase III*, and the free strand stays away from the surface to maximize its entropy. This phase is characterized by $\langle x_2\rangle/N \to 1$ and $\langle x_1\rangle/\sqrt{N} \to 1$ as $N \to \infty$. *This phase is called* $\mathrm{U_{dd}}$.

Depending on the relative strength of the binding energy, ϵ_w, and the pairing energy ϵ_b, we can either have all the four phases listed above, or a few of them, in the phase diagram. We have four parameters: g, T, ϵ_w and ϵ_b. Out of them we can construct three dimensionless quantities $g \to g/\epsilon_\mathrm{b}$, $T \to k_\mathrm{B}T/\epsilon_\mathrm{b}$ and $\epsilon_\mathrm{w} \to \epsilon_\mathrm{w}/\epsilon_\mathrm{b}$. Therefore, without loss of generality, we chose $\epsilon_\mathrm{b} = 1$. The phase of the DNA, for the given set of parameters, can be read from a 3-dimensional g-T-ϵ_w surface. Since it is difficult to show a 3-dimensional plot, we show the cross-sections (g-T plane) of the above surface for various ϵ_w. These are shown in Fig. 8.

Before discussing the phase diagrams in detail, let us do a zero temperature ($T = 0$) analysis of the problem, keeping ϵ_b constant. The energies of the three phases, namely $\mathrm{Z_a}$, $\mathrm{Z_d}$, and $\mathrm{U_{ad}}$ are respectively given by

$$E_{\mathrm{Z}_a} = -N(\epsilon_\mathrm{w}/2 + 1), \tag{25a}$$

$$E_{\mathrm{Z_d}} = -N(g + 1), \tag{25b}$$

and

$$E_{\mathrm{U}_{ad}} = -N(\epsilon_\mathrm{w}/2 + g). \tag{25c}$$

For $1 < \epsilon_\mathrm{w} < 2$, the phase $\mathrm{U_{ad}}$ is always unstable (i.e. it has higher energy). The transition from phase $\mathrm{Z_a}$ to phase $\mathrm{Z_d}$ occurs at $g = \epsilon_\mathrm{w}/2$. But for $\epsilon_\mathrm{w} > 2$, $\mathrm{Z_d}$ is not possible. At $\epsilon_\mathrm{w} = 2$, there is a degeneracy for $\mathrm{Z_d}$ and $\mathrm{U_{ad}}$, which occurs at $g = \epsilon_\mathrm{w}/2$. Therefore at this point all the three phases coexist and it is a triple point.

1. $0 < \epsilon_\mathrm{w} \le 1$ *and* $1 < \epsilon_\mathrm{w} < 2$

When $0 < \epsilon_\mathrm{w} \le 1$, the phase diagram contains three phases, namely $\mathrm{Z_a}$, $\mathrm{Z_d}$ and $\mathrm{U_{dd}}$. But, for $1 < \epsilon_\mathrm{w} < 2$, a new phase, $\mathrm{U_{ad}}$, also appears in the phase diagram. The phase boundary separating $\mathrm{Z_a}$ from $\mathrm{Z_d}$ which decreasing monotonically for $\epsilon_\mathrm{w} < 1$ now shows reentrance at intermediate temperatures. Apart from this feature, there is a region in the phase diagram which involves three phases, namely $\mathrm{Z_d}$, $\mathrm{U_{ad}}$ and $\mathrm{U_{ad}}$. The transition from phase $\mathrm{Z_d}$ to $\mathrm{U_{ad}}$ and $\mathrm{U_{dd}}$ are of first order, whereas, the transition from phase $\mathrm{U_{ad}}$ to phase $\mathrm{U_{dd}}$ is a second order. The second order phase boundary terminates on the first order line at a critical end point. These are discussed in Ref. [37].

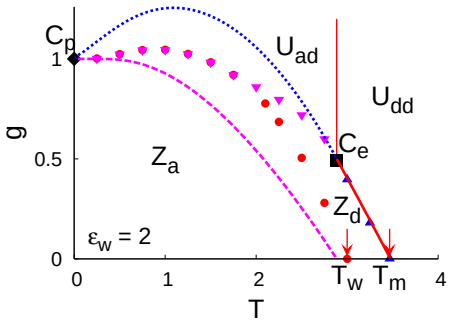

FIG. 8: g vs T phase diagrams for $\epsilon_\mathrm{w} = 2$. The points are obtained by using the exact transfer matrix and T_w, and T_m (shown by arrows) represent respectively the temperature at which the dsDNA desorbs from the surface, and the melting temperature of the DNA. The triple point and the critical end point are shown by a diamond and a square and represented respectively by $\mathrm{C_p}$ and $\mathrm{C_e}$. The thick dashed, solid and dotted lines are respectively Eqs. (8), (21) and (26) and are approximation to the phase boundaries represented by circles, up triangles and down triangles.

2. $\epsilon_\mathrm{w} = 2$: *triple point and critical end point*

The phase diagram for $\epsilon_\mathrm{w} = 2$ is shown in Fig. 8. It contains all the four phases, namely $\mathrm{Z_a}$, $\mathrm{Z_d}$, $\mathrm{U_{ad}}$, and $\mathrm{U_{dd}}$, same as $1 < \epsilon_\mathrm{w} < 2$ case. The phase boundary separating phase $\mathrm{Z_a}$ from phase $\mathrm{Z_d}$ is shown by circles. For comparison, we have also shown, by the dashed line, the phase boundary (see Eq. (8)) for the unzipping of an adsorbed polymer from the straight hard-wall. At low T, the two strands of the DNA, which are bound to each other, behave like a single chain, and therefore, the low-T phase boundary for both the problems match with $g(T = 0) = \epsilon_\mathrm{w}/2$. As T is increased, bubbles form on the DNA. These bubbles create an entropic hindrance on the free strand to stay away from the surface. As a result desorption of dsDNA from the surface occur at a temperature higher than the temperature needed to desorb a single polymer i.e. $T_\mathrm{w} > \epsilon_\mathrm{w}/\ln 2$. The boundary separating phase $\mathrm{Z_d}$ with phase $\mathrm{U_{dd}}$, which is shown by a solid line, is again given by Eq. (24), i.e., it is same as the phase boundary between the zipped and the unzipped phases for $\epsilon_\mathrm{w} = 0$ case. Therefore, in this region, the surface plays no role in determining the phase boundary between the zipped and the unzipped phases. The transition from phase $\mathrm{Z_d}$ to $\mathrm{U_{ad}}$, which is well approximated by

$$g(T) = \frac{k_\mathrm{B}T}{2} \ln\left(\frac{2\sqrt{e^{-\beta\epsilon_\mathrm{w}} - e^{-2\beta\epsilon_\mathrm{w}}} - e^{-\beta\epsilon_\mathrm{b}}}{e^{-\beta\epsilon_\mathrm{b}} - \sqrt{e^{-\beta\epsilon_\mathrm{w}} - e^{-2\beta\epsilon_\mathrm{w}}}}\right), \tag{26}$$

for the $\epsilon < 2$ case (see Appendix A and Ref. [37]) is shown by the dotted lines. This curve deviates markedly with the data obtained by the exact transfer matrix calculations at intermediate temperatures, but still matches in both the high and the low temperatures. This deviation is because we can no longer neglect the effect of surface on the pulled strand mediated via the free strand and the approximation on which the Eq. (26) is based breaks down. At low temperature side, it meets with the dashed line at $T = 0$, showing that the three phases coexist there as expected from zero temperature analysis discussed above. This is the triple point ($T_{\rm p} = 0$) which is shown by $C_{\rm p}$ (filled diamond) in the phase diagram. The numerics, however, cannot resolve the two phase boundaries at low temperatures. On the high temperature side, the dotted curve meets with the solid line with the same slope but with different curvature at the CEP which is shown by $C_{\rm e}$ (filled square). At this point the boundary separating phases $U_{\rm ad}$ and $U_{\rm dd}$ gets terminated.

3. $\epsilon_{\rm w} > 2$

When $\epsilon_{\rm w}$ is slightly greater than 2, the triple point is at a finite temperature ($T_{\rm p} > 0$). However, it is difficult to get the exact location of the triple point because of the difficulty in resolving the phase boundaries at low temperatures. On increasing $\epsilon_{\rm w}$ further, the region representing phase $Z_{\rm d}$ shrinks rapidly and both the triple point and the CEP shift towards higher temperature and disappear independently from the phase diagram. When $\epsilon_{\rm w} = \infty$, the free strand, which remains adsorbed on the surface at all temperatures, acts like a zig zag hard-wall studied in Sec. III. In this case, only the phase $Z_{\rm a}$ and the phase $U_{\rm ad}$ survive in the phase diagram as shown in Fig. 2. This picture is true only in $D = 1 + 1$ dimensions. In $D = 2 + 1$ dimensions the winding of chains will produce dynamic hindrance to unzipping unless torque releasing mechanism is provided at the anchored point. Same will be true for a real DNA, where its helical structure will prevent its unzipping though topoisomerases may help in releasing the extra strain. There is also the possibility of dynamic hindrance leading to nonequilibrium long lived states. These are beyond the scope of this work.

VII. CONCLUSIONS

In this paper, we have studied the unzipping of a dsDNA by pulling a single strand. We find that a dsDNA can be unzipped, even by pulling a single strand, if the pulling force exceeds the critical value. The origin of this transition is different from the unzipping of DNA by pulling its strands in opposite directions. In contrast to the latter case, where the unzipping is possible at all temperatures below the denaturation temperature of the DNA, the unzipping only starts above some minimum temperature ($T_{\rm u} = \epsilon_{\rm b}/\ln 2$) for the single strand pulling but takes place up to the denaturation temperature. For both the cases, the transition is first order.

On introducing the binding energy, $\epsilon_{\rm w}$, at the surface, the phase diagram becomes very rich, with a total of four possible phases. Depending upon the relative strength of $\epsilon_{\rm w}$ and $\epsilon_{\rm b}$, we can either have all the four phases, or a few of them, in the phase diagram. We find that for a wide range of $\epsilon_{\rm w}$, there is a critical end point in the phase diagram, where a line of second order (critical line) terminates on a first order phase boundary. Furthermore, for a narrow range of $\epsilon_{\rm w}$, we have a triple point in the phase diagram. As $\epsilon_{\rm w} \to \infty$, the problem reduces to the unzipping of a polymer, which is adsorbed on a zig zag hard-wall. It seems that the unzipping of an adsorbed dsDNA by pulling a single strand can be a potential candidate to explore the critical end point in single molecule experiments.

APPENDIX A: EXACT PHASE BOUNDARIES

In this appendix we give details of the analytical calculation for obtaining the phase boundaries by using the recursion relation given by Eq. (21). We define the generating function of the partition function $d_n(x)$ by

$$G(z,x) = \sum_{n=0}^{\infty} z^n d_n(x), \tag{A-1}$$

which can be taken of the form (ansatz)

$$G(z,x) = \lambda^x(z) A(z), \tag{A-2}$$

where $\lambda(z)$ and $A(z)$ need to be determined. Using this ansatz in Eq. (21) (z dependence of λ and A suppressed) we get

$$\frac{A}{z} = \left[\left\{e^{\beta g} + e^{-\beta g}\,(1+\lambda)\right\} A + \frac{1}{z}\right] e^{\beta\epsilon_{\rm b}} \quad \text{for } x = 0, \tag{A-3a}$$

and

$$\frac{\lambda^x}{z} = \lambda^{x-1}\,(1+\lambda)\left[e^{\beta g} + \lambda e^{-\beta g}\right] \quad \text{for } x > 0, \tag{A-3b}$$

from which one obtains

$$\lambda = \frac{1}{2z}\Big[e^{\beta g} - \left(e^{2\beta g}+1\right) z + \sqrt{\left\{\left(e^{2\beta g}+1\right) z - e^{\beta g}\right\}^2 - 4z^2 e^{2\beta g}}\Big], \tag{A-4a}$$

and

$$A = \frac{e^{\beta\epsilon_{\rm b}}}{1 - z\left[e^{\beta g} + e^{-\beta g}\,(1+\lambda)\right] e^{\beta\epsilon_{\rm b}}}. \tag{A-4b}$$

Now from Eqs. (A-1) and (A-2), we have

$$G(z) = \sum_x G(z,x) = \sum_x \lambda^x A = \frac{A}{1-\lambda}, \tag{A-5}$$

which has a singularity at $\lambda = 1$. Substituting $\lambda = 1$ in Eqs. (A-4a) and (A-4b), we get singularities of the unzipped and the zipped phases respectively as

$$z_4 = \frac{1}{4\cosh\beta g} = \left(\frac{1}{2}\right)\left(\frac{1}{2\cosh\beta g}\right), \quad \text{(A-6a)}$$

and

$$z_2 = \frac{e^{-\beta\epsilon_b}}{e^{\beta g} + 2e^{-\beta g}}. \quad \text{(A-6b)}$$

The first factor in Eq. (A-6a) is the contribution of the random walk of the free strand when the DNA is in the unzipped phase and the second factor is the contribution of the force on the pulled strand. The phase boundary separating the zipped and the unzipped phases is given by $z_2 = z_4$, which reads as

$$g(T) = \frac{k_B T}{2}\ln\left(\frac{2e^{-\beta\epsilon_b} - 2}{1 - 2e^{-\beta\epsilon_b}}\right). \quad \text{(A-7)}$$

The zero force limit (i.e. $g \to 0$) of Eq. (A-7) gives the thermal melting temperature of the dsDNA. This gives

$$T_m = \frac{\epsilon_b}{\ln\ 4/3}. \quad \text{(A-8)}$$

In the opposite limit (i.e. $g \to \infty$), we obtain the minimum temperature

$$T_u = \frac{\epsilon_b}{\ln 2}, \quad \text{(A-9)}$$

above which the dsDNA can be unzipped by pulling a single strand.

By using the same analysis given above, we can also approximate the phase boundaries between the zipped and the unzipped phases in the presence of an attractive surface with energy $-\epsilon_w$ near DNA. By maintaining the structure of the singularity z_4, the singularity which contribute to the partition function of phase U_{ad} in the thermodynamic limit can be approximated as

$$z_3 = \left(\sqrt{e^{-\beta\epsilon_w} - e^{-2\beta\epsilon_w}}\right)\left(\frac{1}{2\cosh\beta g}\right). \quad \text{(A-10)}$$

In Eq. (A-10), the first factor is the contribution of the adsorbed free strand on the surface and the second factor is same as in Eq. (A-6a). The phase boundary separating phase Z_d with phase U_{ad} is given by

$$g(T) = \frac{k_B T}{2}\ \ln\left(\frac{2\sqrt{e^{-\beta\epsilon_w} - e^{-2\beta\epsilon_w}} - e^{-\beta\epsilon_b}}{e^{-\beta\epsilon_b} - \sqrt{e^{-\beta\epsilon_w} - e^{-2\beta\epsilon_w}}}\right), \quad \text{(A-11)}$$

which is obtained by equating z_4 with z_2. This phase boundary is shown by dotted lines in Fig. 8. The approximation done in Eq. (A-10) is valid only for smaller values of ϵ_w and breaks as ϵ_w becomes comparable to ϵ_b as evident from Fig. 8(b) and (c). However, the $g \to \infty$ limit of Eq. (A-11) gives the T_u and ϵ_w dependence as

$$\epsilon_w = k_B T_u\ \ln\left[\frac{2}{1 - \sqrt{1 - 4\exp\left(-2\epsilon_b/k_B T_u\right)}}\right], \quad \text{(A-12)}$$

from which one obtains $T_u \to \epsilon_b/\ln 2$ as $\epsilon_w \to 1$ and $T_u \to 0$ as $\epsilon_w \to 2$.

APPENDIX B: DETAILS OF MOTE CARLO SIMULATIONS

In this appendix we give the details of Monte Carlo simulations used in obtaining the force-distance isotherms in both $1+1$ and $2+1$ dimensions. We model the bases of the DNA by beads and the two adjacent beads on a strand, are connected by a rigid rod of unit length which stays on edges of the square or the cubic lattice in $1+1$ and $2+1$ dimensions respectively. If the beads of the two strands are unit distance apart, there is a binding between them. At the diagonal of the square and the cube there is an impenetrable surface. One end of both the chains are anchored at the origin and a pulling force g is applied on the bead at the free end of the pulled chain. We consider a single bead flip dynamics. In $1+1$ dimensions, the jth bead in the interior of the strand, e.g. the free strand, located at a distance x_{1_j} from the surface (state μ), is flipped to $x'_{1_j} = x_{1_j} \pm 2$ (state ν), provided $x_{1_{j+1}} - x'_{1_j} = x'_{1_j} - x_{1_{j-1}} = 1$. This constraint ensures that the chain does not break while doing the dynamics. The move is accepted (or rejected) according to the rule

$$P(\mu \to \nu) = \begin{cases} e^{-\beta(E_\nu - E_\mu)} & \text{if} \quad E_\nu - E_\mu > 0 \\ 1 & \text{otherwise.} \end{cases} \quad \text{(B-1)}$$

The same thing has to be repeated for the pulled strand also. For the end bead we have to take care of the energy contribution $g(x'_{2_N} - x_{2_N})$ due to the force g. In $2+1$ dimensions, the bead can be flipped in three positions without breaking the chain. Apart from the connectivity constraint, the excluded volume effects, between the strands and between the free strand and the surface, have to be taken care of. This means the following moves have to be rejected while doing the dynamics (i) the free chain crossing the pulled chain, (ii) the free chain crossing the surface on which it is adsorbed, and (iii) the pulled chain crossing the first chain. It is possible for the DNA to reach any state from any other state using the above moves. The $2N$ such flips, N for each strand, constitutes one Monte Carlo step (MCS) per bead. At each value of the force, where the simulation is performed, we allow the system to equilibrate by repeating the above procedure for 10^6 MCS and start measurements only after it. Between any two measurements we run the procedure, without doing measurements, for 10^3 MCS to avoid correlations between two measurements.

We have performed $K = 7$ simulations at $\beta = 2/3$ at various g as indicated in Fig. 7(b). The expectation value of $\langle x_{1,2}\rangle$ is obtained by averaging over 10^6 MCS. Other than the averaged values, we have also obtained histograms, $h_k(E, x_1, x_2)(k = 1, \ldots K)$ of the energy E (binding from the surface plus base pairing but not the contribution from the force), the positions of the end monomers for the free and the pulled strands represented by x_1 and x_2 respectively. The kth histogram is collected at force g_k with n_k number of states. By using the multiple histogram technique [44], the average distance (from the surface) of the last monomers of both strands, $\langle x_{1,2}\rangle$ at force g is given by

$$\langle x_{1,2}(\beta, g)\rangle = \frac{1}{Z(\beta, g)} \sum_{E,x_1,x_2} x_{1,2}\ e^{-\beta(E-gx_2)} \frac{\sum_{j=1}^{K} h_j(E, x_1, x_2)}{\sum_{j=1}^{K} n_j Z_j^{-1} e^{-\beta(E-g_j x_2)}}, \tag{B-2}$$

where

$$Z(\beta, g) = \sum_{E,x_1,x_2} e^{-\beta(E-gx_2)} \frac{\sum_{j=1}^{K} h_j(E, x_1, x_2)}{\sum_{j=1}^{K} n_j Z_j^{-1} e^{-\beta(E-g_j x_2)}}, \tag{B-3}$$

is an approximate partition function at g, estimated using Z_k, i.e., the partition functions at g_k. The partition functions Z_k are obtained self-consistently from the following equation

$$Z_k = \sum_{E,x_1,x_2} e^{-\beta(E-g_k x_2)} \frac{\sum_{j=1}^{K} h_j(E, x_1, x_2)}{\sum_{j=1}^{K} n_j Z_j^{-1} e^{-\beta(E-g_j x_2)}}. \tag{B-4}$$

We iterate the above equation with starting values $Z_k = 1$ for all k. The convergence is monitored by estimating the amount of change after each iteration. We gauged it by calculating the quantity

$$\Delta^2 = \sum_k \left[\frac{Z_k^{(m)} - Z_k^{(m-1)}}{Z_k^{(m)}}\right]^2, \tag{B-5}$$

where $Z_k^{(m)}$ is the value of Z_k at the mth iteration. When this quantity falls below some predefined quantity ϵ^2, the convergence is achieved. We take $\epsilon^2 = 10^{-14}$. The force-distance isotherms obtained by this procedure in $1 + 1$ dimensions is shown in Fig. 7(b).

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